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(54) **Catalyst for use in preparation of pyromellitic acid and/or pyromellitic anhydride.**

(57) A supported catalyst on an inert carrier suitable for the preparation of pyromellitic acid or its anhydride by catalytic vapor phase oxidation of a tetra- C_1 —C_4 alkylbenzene, said catalyst comprising catalytically active material composed of 1 to 20 parts by weight of V_2O_5, 99 to 80 parts of weight of TiO_2 and/or SnO_2 and/or ZrO_2, and per one hundred parts by weight of V_2O_5, TiO_2 and/or SnO_2 and/or ZrO_2, 0.02 to 10 parts by weight, calculated as P_2O_5, of a phosphorus compound, 0.01 to 5 parts by weight, calculated as Nb_2O_5, of a niobium compound, 0 to 1.2 parts by weight, calculated as oxide, of at least one metal selected from the group consisting of potassium, cesium, rubidium and thallium, and 0 to 10 parts by weight, calculated as Sb_2O_3, of an antimony compound, and an inert carrier supporting said catalytically active material thereon.

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This Invention relates to a suitable catalyst for use in the preparation of pyromellitic acid and/or pyromellitic anhydride by vapor phase catalytic oxidation of a tetra-C_1-C_4-alkylbenzene such as durene with air or a molecular oxygen-containing gas.

Vapor-phase catalytic oxidation of tetra-C_1-C_4-alkylbenzenes such as durene with air or a molecular oxygen-containing gas is one of the industrial methods to obtain pyromellitic acid or pyromellitic anhydride. Although a number of catalysts have been proposed for this oxidation process, none of them have proved to have satisfactory performances. For instance, the catalysts proposed in Japanese Patent Publications Nos. 20302/1974 and 31972/1974 show relatively high yields in the preparation of pyromellitic anhydride by vapor phase oxidation of durene. However, these high yields are achieved only under the conditions of a very low concentration of durene in a feed gas and of a very high space velocity. To use catalysts which have to be operated under such conditions is disadvantageous for the industrial oxidation process because the lower ratio of durene/air requires more energy to send a reaction gas to a reactor and higher space velocities result in an increased pressure drop of the catalyst bed.

The industrial oxidation process where the concentration of a hydrocarbon to be oxidized in a feed gas is extremely low has another problem that a heat medium surrounding catalyst packed tubes in a reactor has to be heated by an external heating apparatus in order to maintain an optimum reaction temperature because the latent heat of the feed gas through the reactor exceeds the total oxidation heat of the hydrocarbon.

On the other hand, it is generally considered advantageous for industrial practice to use catalysts at

higher space v locities becaus the catalyst volume needed becomes smaller. However, in a practical multi-tub r actor the catalyst bed packing length must be more than 1,000 mm, preferably more than 1,500 mm in view of the reactor design and a heat removal system for the reactor. For this reason, there is a limitation in decreasing the catalyst volume in a tube of a practical industrial reactor, and the pressure drop of a catalyst bed becomes extremely high as the linear velocity of the gas in the tube is very high at such a high space velocity. As above said, the catalytic oxidation reaction carried out under the conditions of low concentrations of a hydrocarbon to be oxidized in a feed gas and of high space velocities is not always economical in a commercial operation because it leads the increase of steam or electricity in loading on an air blower or compressor.

Accordingly, the objective of this invention is to provide catalysts for the preparation of pyromellitic acid and/or pyromellitic anhydride by the vapor phase fixd bed catalytic oxidation of a tetra-C_1-C_4-alkylbenzene such as durene with air or a molecular-oxygen-containing gas which have a high selectivity to pyromellitic acid and/or pyromellitic anhydride and high heat durability in an operation under high loading conditions of high ratios of the tetra-alkylbenzene/air or molecular oxygen-containing gas, 20-60 g/NM^3, and of relatively low space velocities of 1,000-10,000 hr^{-1}.

As a result of investigations on the improvement of the heat durability of catalysts, we have found that a specific supported catalyst on an inert carrier, especially an inert porous carrier, is suitable for the purpose of this invention and this specific catalyst comprises a catalytically active material composed of vanadium pentoxide, titanium dioxide and/or zirconium dioxide and/or stannic dioxide and some other specific ingredients.

It has also been found that the addition of a specific amount of an antimony compound is advantageous for

the lif of the catalyst because the optimum operating temperature f the catalyst is l w r than that of the catalyst without addition of the antimony compound.

This invention is specified as follows:

(1) Supported catalysts on an inert carrier suitable for the preparation of pyromellitic acid or its anhydride by catalytic vapor phase oxidation of a tetra-C_1-C_4-alkylbenzene, said catalyst comprising a catalytically active material composed of 1-20 parts by weight of V_2O_5, 99-80 parts by weight of TiO_2 and/or SnO_2 and/or ZrO_2, and per one hundred parts by weight of V_2O_5, TiO_2 and/or SnO_2 and/or ZrO_2 combined, 0.02 to 10 parts by weight, calculated as P_2O_5, of a phosphorus compound, 0.01 to 5 parts by weight, calculated as Nb_2O_5, of a niobium compound, 0 to 1.2 parts by weight, calculated as oxide, of at least one metal selected from the group consisting of potassium, cesium, rubidium and thallium, 0 to 10 parts by weight, calculated as Sb_2O_3, of an antimony compound, and an inert carrier supporting said catalytically active material thereon.

(2) Supported catalysts according to the description (1) where the weight ratio of TiO_2/SnO_2 is less than 4.

(3) Supported catalysts according to the description (1) where the weight ratio of TiO_2 and/or SnO_2/ZrO_2 is less than 4.

Titanium dioxide which is suitable for this invention is anatase prepared by either the pyrolysis of ammonium titanyl sulfate, the calcination of titanium hydroxide obtained by hydrolysis of titanium sulfate, the vapor phase oxidation of titanium tetrachloride, or another method. Porous anatase of which particle size is 0.4-0.7 micron and specific surface area is 10-60 m^2/g obtained by the calcination of titanium hydroxide is used especially preferably.

As stannic dioxide for the purpose of the invention SnO_2 prepared by the previous calcination of a stannic

or stannous compound as sulfate, nitrate, carbonate and so on is preferably used and SnO_2 obtained by calcination of stannous sulfate at a temperature of 600-900^oC for 2-10 hours and having a particle size of 0.01-1 micron and a specific surface area of 5-100 m^2/g, especially 8-60 m^2/g, is used especially preferably.

As zirconium dioxide ZrO_2 obtained by the calcination of a zirconium compound as sulfate, nitrate, and so on is preferably used and ZrO_2 prepared by the calcination of zirconyl nitrate at a temperature of 600-900^oC for 2-10 hours and having a particle size of 0.01-1 micron and a specific surface area of 5-100 m^2/g, especially 8-60 m^2/g, is used especially preferably.

The catalyst of the present invention is of the composition comprising V_2O_5, TiO_2 and/or SnO_2 and/or ZrO_2, P_2O_5, Nb_2O_5 and optionally Sb_2O_3 and optionally at least one metal oxide selected from the group consisting of K_2O, Cs_2O, Rb_2O and Tl_2O and further optionally, per 100 parts by weight of V_2O_5 and TiO_2 and/or ZrO_2 and/or SnO_2, 0.01-3 parts by weight of at least one compound of the group consisting of CaO, SrO, BaO, ZnO and rare earth element oxides. The term "rare earth element" used in this specification means elements of atomic number 39 and of atomic number 57-71 and preferably Y, La, Ce, Nd, Gd, Tb and Er are used.

The V_2O_5, Nb_2O_5, P_2P_5, Sb_2O_3, K_2O, Cs_2O, Tl_2O, Rb_2O, CaO, SrO, BaO, ZnO and rare earth element oxides used in the catalyst of the present invention may be adequately chosen from oxides, ammonium salts, nitrates, sulfates, halides, carbonates, hydroxides, organic acid salts and other compounds derived from such elements. That is to say, the components of the catalysts of the present invention are not restricted to the oxides as described in this specification, which indicate merely the compositions of integral constituents in the finished catalyst.

As the carriers, ordinary inert inorganic

substances are used for the catalyst of th invention, but suitable porous inert carriers are those having an apparent porosity of 5-50%, a specific surface area of less than 5 m^2/g, preferably less than 1 m^2/g, a silicon carbide content of more than 50% by weight, preferably more than 80% by weight and an aluminum content calculated as Al_2O_3 of less than 10% by weight, prefertably less than 3% by weight. Accordingly, self-bonded silicon carbide having a purity of more than 98% is also suitably used for this invention.

The form of the carrier is not limited and a sphere-, ring-, pellet-, conical-, or saddle-type carrier with an external diameter of 3-15 mm is suitably used.

The supporting of catalytically active material onto the surface of the carrier is carried out by any conventional methods such as penetration or spraying, and preferably by the method of spraying a catalyst slurry onto the carrier heated to 150-250°C.

3-50 g, preferably 5-15 g of the catalytically active material is supported on 100 cc (apparent volume) of the carrier.

And in the catalyst thus obtained, the total volume of pores having a diameter of 0.15 to 0.45 micron present in the layer of the catalytically active material on the carrier is at least 50%, preferably at least 70%, of that of pores having a diameter of not more than 10 mcirons present in said layer of the catalytically active material.

Generally, in the case of using a catalyst continuously for a long period of time, the catalytically active material drops off from the surface of the carrier to an increasing extent as the amount of the tetra-alkylbenzene loaded increases. Furthermore, a catalyst is generally preferred by spraying or impregnating a homogenized solution or slurry of the catalytically active material on or in a carrier having high mechanical strength. Since the supporting strength of the catalytically active material is based on a chemical and/or a

physical bonding force between the catalytically active material and the carrier, the amount of the catalytically active material to be deposited on the carrier is naturally limited. If it is small, the catalyst has low activity. Even when a catalyst can be obtained which has sufficient activity and contains the catalytically active material with industrially sufficient supporting strength, it frequently happens that the ratio of the catalytically active material which can be supported on the carrier is very low to cause large losses of the catalytically active materials occur, and therefore, the productivity is poor.

According to this invention, the above problems can be solved by adding whiskers as a supporting aid to the raw materials for the catalytically active material and thereby supporting the catalytically active material well on the carrier.

Metal whiskers and refractory whiskers can, for example, be used suitably as the supporting aid. Examples include metal whiskers such as tungsten, iron or nickel whiskers, and refractory whiskers such as silicon carbide, silicon nitride, aluminum oxide, titanium carbide or calcium phosphate whiskers. Suitable whiskers have an average diameter of not more than 5 microns, preferably not more than 1 micron, a length of not more than 1,000 microns, preferably not more than 500 microns, and an aspect ratio of from 10 to 500, preferably from 20 to 300.

Deposition of the catalytically active material on the carrier can be carried out by conventional known methods. Specifically, it is carried out, for example, by spraying a solution or slurry containing catalytically active ingredients onto the surface of a carrier preheated to 150 to 250°C, or by impregnating the catalyst solution or slurry in the carrier, and concentrating the solution or slurry to adhere the catalytically active material to the carrier. At this time, the whisker is dispersed in the catalyst solution or slurry in an amount of 1 to 20% by

weight, preferably 3 to 10% by weight, based n the weight of the finished catalyst. The catalytically active mat - rial is supported in a pr portion of 3 to 50 g, preferably 5 to 15 g, per 100 cc of the apparent volume of the catalyst.

The supported catalyst of this invention produced by using the whisker as a supporting aid has the advantage of increased activity and/or selectivity in some catalytic reactions because the space volume of the catalyst-supported layer is increased.

The supported material thus obtained is calcined under an air atmosphere at a temperature of 300-650°C, preferably 400-600°C for 1-10 hours, preferably 2-6 hours to get a finished catalyst.

Conventional methods of lowering the temperature of hot spots which appear in the feed gas side of a catalyst bed can be used in order to decrease the reaction with COx and other side reactions of the tetra-alkylbenzene and pyromellitic anhyride and to minimize a thermal deterioration of the catalyst by local heating. For instance, the hot spot temperature is lowered by controlling the amount of reaction in the feed gas side of the catalyst bed. This can be achieved by a physical method, for example, by diluting the catalyst in the zone with the carrier, replacing the catalyst in the zone with a large-sized one, or using a catalyst in which the supporting ratio of a catalytically active material to a carrier is decreased, and a chemical method, for example, by increasing the content of the alkaline metal compound in the zone, decreasing the content of the phosphorus compound in it, or using a catalyst made from TiO_2 and/or SnO_2 and/or ZrO_2 with a lower surface area.

The catalyst of the present invention is used in a multi-tubular fixed bed reactor surrounded by a fused salt at a temperature of 320-440°C, especially 360-420°C. Each of the tubes has an inside diameter of 15-40 mm, preferably 20-30 mm.

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The catalyst is loaded into the tubes to a height of 1-3.5 meters, especially 1.5-3 meters and a feed gas preheated to 120-160°C comprising durene or another tetra-alkylbenzene and air or a molecular oxygen-containing gas is introduced into a catalyst bed at a space velocity of 1,000-10,000 hr^{-1} with the ratio of durene or another tetra-alkylbenzene to air 20-60 g/NM^3 to obtain pyromellitic anhydride in a yield of 110-120% by weight.

The following examples further illustrate the present invention.

Example 1

$TiCl_4$ of special reagent grade (5,700 g) was added to deionized water to form a 60% aqueous solution, and 2,940 g of sulfuric acid of special reagent grade was added to it with stirring. Separately, a saturated aqueous solution containing 3,940 g of ammonium sulfate of special reagent grade and heated at 100°C was prepared and the saturated solution was stirred into the $TiCl_4$-H_2SO_4 aqueous solution. The mixed solution was allowed to stand still to precipitate ammonium titanyl sulfate $(NH_4)_2SO_4 \cdot TiOSO_4 \cdot H_2O$. The precipitate was filtered and calcined at 750°C for 10 hours to obtain 2,300 g of powdered TiO_2 by thermal decomposition of the ammonium titanyl sulfate.

Oxalic acid (514 g) was dissolved in deionized water to form an aqueous oxalic acid solution. The solution was mixed with 257 g of ammonium metavanadate, 16.2 g of ammonium dihydrogen phosphate and 12.2 g of niobium chloride and thoroughly stirred. To the aqueous solution were added 120 g of antimony trioxide and 1,800 g of aforesaid TiO_2, and the mixture was stirred for 30 minutes to form a slurry of a catalytically active material.

Into an externally heatable rotary drum, 2,000 cc of a spherical SiC carrier having an average diameter of 5 mm, an SiC content of 98.5%, and an apparent porosity of 20% was introduced, and preheated to 200-250°C.

180 g of the catalytically active material was

supported on the surface of the carrier by spraying the catalyst slurry onto the carrier while rotating the drum, and subsequently the contents in the drum were calcined at 530°C for 8 hours under an air atmosphere to obtain a supported catalyst containing V_2O_5 and TiO_2 in a weight ratio of 10:90 and based on the total weight of V_2O_5 and TiO_2, 0.5% by weight of P_2O_5, 0.3% by weight of Nb_2O_5 and 6% by weight of Sb_2O_3.

The measurement of the pore distribution of the catalyst thus obtained by the mercury penetration method showed the pore volume occupied by pores with a diameter of 0.05-0.45 micron was 89% of the total volume of pores having a diameter of less than 10 microns.

100 cc of the catalyst was loaded in a stainless tube with an internal diameter of 25 mm immersed in a salt bath maintained at 390°C. Oxidation reaction was carried out by passing hourly 15 g of durene and 500 N-liters of air through the catalyst bed and the product gas was introduced into a crystal collector and a scrubbing vessel.

Analysis of products by liquid chromatography showed that the yield of pyromellitic anhydride was 113.2% by weight.

Example 2

A titanium sulfate solution was prepared by mixing ilmenite with 80% sulfuric acid, allowing them to react fully with each other, diluting the reaction product with water to form an aqueous solution of titanium sulfate, adding iron fragments, reducing iron in the ilmenite, and cooling the product to precipitate and separate ferric sulfate. Hydrous titanium dioxide was prepared by the hydrolysis of the thus obtained titanium sulfate solution while blowing steam kept at 150-170°C. Hydrous titanium dioxide was calcined under an air atmosphere at 800°C for 4 hours and pulverized by a jet stream crusher to obtain porous anatase TiO_2 having a particle size of about 0.5 micron and a specific surface area of 22 m^2/g.

Oxalic acid (1,030 g), 515 g of ammonium metavanadate, 25.9 g of ammonium dihydrogen phosphate, 20.3 g of niobium chloride and 3.4 g of barium nitrate were dissolved in 6400 cc of deionized water and 200 g of antimony trioxide and 1,600 g of TiO_2 above prepared were suspended in the solution, and the suspension was homogenized for 30 minutes to get a catalyst slurry.

A catalyst having the catalytic composition, $V_2O_5:TiO_2:P_2O_5:Nb_2O_5:Sb_2O_3:BaO$ = 20:80:0.8:0.5:10:0.1 by weight, was prepared by the same method as described in Example 1. The volume occupied by pores having a diameter of 0.05-0.45 micron was 86% of the total volume of pores having a diameter of less than 10 microns.

Pyromellitic anhydride was obtained on the catalyst in a yield of 114.1% by weight under the same conditions as in Example 1 except that the salt bath temperature was changed to 400°C.

Examples 3-6

Catalysts shown in Table 1 were prepared by the same method as in Example 1 and their performances were shown in Table 2.

Table 1

Example	Catalyst composition (weight ratio)
	V_2O_5:TiO_2:Nb_2O_5:P_2O_5:Sb_2O_5
3	10 : 90 : 0.5 : 0.8 : 15 : 0.25(Cs_2O) : 0.3(SrO) : 0.1(CeO_2)
4	60 : 40 : 0.3 : 0.5 : 6 : 0.1(Rb_2O) : 0.08(Tb_4O_7)
5	10 : 90 : 0.8 : 0.8 : 10 : 0.07(Tl_2O) : 0.3(Zn)
6	25 : 75 : 0.5 : 1.5 : 8 : 0.1(Gd_2O_3)

Table 2.

Example	N.T. (^{o}C)	Space velocity (hr^{-1})	Durene concentration (g/NM^3)	Yield calculated for pyromellitic anhydride (wt%)
3	390	8000	25	114.5
4	390	6000	35	110.2
5	400	8000	30	112.9
6	390	5000	30	113.3

Example 7

SnO_2 having an average diameter of 0.18 micron and a specific surface area of 18 m^2/g was obtained by calcining stannous sulfate at 800°C for 4 hours and pulverizing it by a jet stream crusher.

Oxalic acid (200 g), 121.8 g of ammonium metavanadate, 15.35 g of ammonium dihydrogen phosphate, 19.27 g of niobium chloride and 5.24 g of cesium nitrate were dissolved in 6,400 cc of deionized water and 1,800 g of aforesaid SnO_2 was suspended in the solution. The suspension was homogenized to obtain a catalyst slurry.

Into an externally heatable rotatory drum 2,000 cc of a pelletized SiC (5 mm x 6 mm L, specific surface area 0.4 m^2/g) was introduced and preheated to 150-200°C. 180 g of the catalytically active material was supported on the carrier by spraying the catalyst slurry on it while rotating the drum to get catalyst-A.

Separately, catalyst-B was obtained by the same method as in the preparation of catalyst-A except that the amount of ammonium dihydrogen phosphate was changed to 27.63 g.

Into an iron tube (diameter 25 mm, length

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3.5 met rs) immersed in a salt bath maintained at 410°C, catalyst-B was first loaded to a height of 1.5 meters and subsequently catalyst-A was loaded to a height of 1.5 meters on the catalyst-B.

From the top of the tube a mixed gas preheated to 140°C and having a durene/air ratio of 30 g/NM^3 was introduced at a space velocity of 4,000 hr^{-1} to obtain pyromellitic anhydride in a yield of 113.4% by weight.

Example 8

A hydrogen chloride solution (200 cc), 10 g of vanadium pentoxide, 1.62 g of ammonium hydrogen phosphate and 0.28 g of potassium sulfate were dissolved in 800 cc of deionized water. Stannous sulfate (42.74 g) and 60 g of porous anatase TiO_2 (diameter 0.5 micron, specific surface area 60 m^2/g) were suspended in the solution, and the suspension was homogenized by a mixer to obtain a catalyst slurry.

Into an externally heatable evaporating dish the slurry obtained above and 1,000 cc of a spherical carrier (diameter 6 mm, specific surface area 0.3 m^2/g, apparent porosity 48%) comprising 75% by weight of SiC, 17% by weight of SiO_2, and 8% by weight of Al_2O_3 were introduded and heated to dryness under mixing to support 160 g of the catalytically active material on the carrier. The contents of the dish were calcined at 580°C for 8 hours to obtain a catalyst.

In a carbon steel tube (diameter 20 mm, 3.5 meters L) immersed in a salt bath maintained at 405°C, a mixed gas having a durene/air ratio of 40 g/NM^3 was introduced at a space velocity of 3,000 hr^{-1} to obtain pyromellitic anhydride in a yield of 112.1% by weight.

Example 9

Oxalic acid (120 g), 55.7 g of vanadium pentoxide, 56.1 g of niobium chloride, 9.02 g of ammonium dihydrogen phosphate, 7.2 g of rubidium sulfate and 2.33 g of thallium sulfate were dissolved in 6,400 cc of deionized

water, and 930 g f SnO_2 used in Exampl 7 and 870 g of TiO_2 used in Example 8 were suspended in the solution, and the suspension was homogenized by mixer to obtain a catalyst slurry.

Into an externally heatable rotatory drum 2,000 cc of a ring-type carrier (apparent porosity 40%, external diameter 7 mm, internal diameter 4 mm, length 7 mm) comprising 10% by weight of magnesium silicate, 20% by weight of SiO_2, and 70% by weight of SiC was introduced and preheated to 150-200°C. 150 g of the catalytically active material was supported on the carrier by spraying the slurry on it under rotating and the contents of the drum were calcined at 500°C for 4 hours to obtain catalyst-C.

Separately, catalyst-D was prepared by the same method as in the preparation of catalyst-C except that rubidium sulfate and thallium sulfate were not added.

Into a carbon steel reactor (ID = 25 mm, L = 3.5 mm) immersed in a salt bath maintained at 380°C, catalyst-D was first loaded to a height of 1,000 mm and onto it catalyst-C was loaded to a height of 1,000 mm.

From the top of the tube a mixed gas of durene and a molecular oxygen-containing gas (oxygen 10% by volume, steam 10% by volume, nitrogen 80% by volume) of which the ratio of durene/molecular oxygen-containing gas was 40 g/NM^3 was introduced at a space velocity of 3,500 hr^{-1} to obtain pyromellitic anhydride of 117.3% by weight.

Example 10

ZrO_2 having a particle size of 0.2 micron and a specific surface area of 25 m^2/g was obtained by calcining zirconyl nitrate at 750°C for 3 hours and pulverized it by a jet stream crusher.

Oxalic acid (200 g), 96.7 g of ammonium metavanadate, 9.1 g of diammonium hydrogen phosphate, 22.9 g of niobium chloride, 3.47 g of potassium hydroxide were dissolved in 6,400 cc of deionized water, and 1,800 g of ZrO_2 above obtained was suspended in the solution. The

suspension was h mogenized by a mixer to get a catalyst slurry.

Into an externally heatable rotatory drum 2,000 cc of a ring-type carrier (ID = 4 mm, OD = 6 mm, L = 6 mm, specific surface area = 0.2 m^2/g) comprising 6% by weight of SiO_2, 2% by weight of Al_2O_3, and 92% by weight of SiC was introduced and preheated to 150-220°C. 180 g of the catalytically active material was supported on the carrier by spraying the catalyst slurry on it while rotating the drum and the contents of the drum were calcined at 540°C for 6 hours to obtain a catalyst.

Into a carbon steel tube (ID = 25 mm, L = 3.5 meters) immersed in a salt bath maintained at 400°C the catalyst was loaded to a height of 2,500 mm. From the top of the tube, a preheated mixed gas having a durene/air ratio of 25 g/NM^3 was introduced at a space velocity of 4,000 hr^{-1}. The initial yield of pyromellitic anhydride was 114.5% by weight and the hot spot temperature was 465°C.

The yield and hot spot temperature after 3 months and 6 months continuation of oxidation reaction under the above conduitions were 114.1% by weight, 466°C (3 months) and 113.3% by weight, 461°C (6 months), respectively. These results show the very stable activity of the catalyst in a long run.

Example 11

Oxalic acid (450 g), 201.4 g of ammonium metavanadate, 23.8 g of niobium chloride, 9.5 g of ammonium dihydogen phosphate, and 3.38 g of cesium nitrate were dissolved in 6,400 cc of deionized water, and 980 g of ZrO_2 (particle size 0.2 micron, specific surface area 25 m^2/g) and 820 g of porous anatase TiO_2 (particle size 0.5 micron, specific surface area 20 m^2/g) were suspended in the solution to obtain catalyst slurry.

Into an externally heatable rotatory drum 2,000 cc of a spherical catalyst (diameter 6 mm, apparent

porosity 43%, surface ara 0.3 m^2/g) c mprising 2% by weight of Al_2O_3, 4% by weight of SiO_2 and 94% by w ight of SiC was introduc d and preheated to 150-200°C.

180 g of the catalytically active material was supported by spraying the catalyst slurry on it. The contents of the drum were calcined at 520°C for 4 hours to obtain catalyst-E.

Separately, catalyst-F was prepared by the same method as in catalyst-E except that ZrO_2 (particle size 0.3 micron, specific surface area 12 m^2/g) and porous anatase TiO_2 (particle size 0.6 micron, surface area 13 m^2/g) were used.

Catalyst-E was first loaded into a tube (ID = 25 mm, 3.5 meters L) immersed in a salt bath maintained at 400°C to a height of 1.5 meters and subsequently catalyst-F was loaded to a height of 1 meter on it.

From the top of the tube a mixed gas having a durene/air ratio of 35 g/NM^3 was introduced at a space velocity of 4,000 hr^{-1} to obtain pyromellitic anhydride in a yield of 115.6% by weight.

Example 12

Oxalic acid (900 g), 408.6 g of ammonium metavanadate, 4.3 g of niobium chloride, 27.4 g of ammonium dihydrogen phosphate, 21.3 g of thallium nitrate were dissolved in 6,400 cc of deionized water and 42.4 g of antimony trioxide, 720 g of ZrO_2 (same to Example 11) and 1,080 g of TiO_2 (same to Example 11) were suspended in the solution to obtain a catalyst slurry.

Into an externally heatable drum 2,000 cc of a spherical self-bonded SiC carrier (diameter 6 mm, apparent porosity 38%, specific surface area 0.2 m^2/g) was introduced and pre-heated to 150-200°C. 170 g of the catalytically active material was supported on the carrier and the contents of the drum were calcined at 580°C for 3 hours to obtain catalyst-G.

Separately, catalyst-H was prepared by the same method as in the preparation of catalyst-G except that

6.68 g of rubidium nitrate was used instead of thallium nitrate.

Catalyst-H was first loaded into a tube (ID = 25 mm, L = 3.5 meters) immersed in a salt bath maintained at 375°C to a height of 1.25 meters and subsequently on it catalyst-G was loaded to a height of 1.25 meters.

From the top of the tube, a mixture of durene and a molecular oxygen-containing gas (oxygen 12%, steam 10%, nitrogen 78%) of which the ratio of durene to the oxygen-containing gas was 40 g/NM^3 was introduced at a space velocity of 3,500 hr^{-1}. The initial yield of pyromellitic anhydride was 117.1% by weight and the hot spot temperature was 457°C.

The salt bath temperature was raised to, and maintained at, 387°C for 1 month so that the hot spot temperature became 500°C. When the salt bath temperature was lowered to 375°C after this period, the yield and hot spot temperature at that time were 116.2% by weight and 452°C, respectively, and no serious thermal deterioration was observed.

Example 13

Oxalic acid (200 g), 96.5 g of ammonium metavanadate, 7.6 g of niobium chloride, 20.7 g of cesium nitrate were dissolved in 6,400 cc of deionized water and 18.8 g of antimony trioxide, 940 g of ZrO_2 (same as that in Example 10) and 470 g of TiO_2 (same as that in catalyst-F of Example 11) and 390 g of SnO_2 obtained by calcination of $SnSO_4$ at 700°C for 4 hours were suspended in the solution to obtain a catalyst slurry.

Into an externally heatable drum 2,000 cc of an interlock saddle-type carrier (apparent porosity 45%, specific surface area 0.4 m^2/g, average length 12 mm, external diameter 5 mm, internal diameter 6 mm, thickness 1 mm) comprising 80% by weight of SiC, 6% by weight of MgO and 14% by weight of SiO_2 was introduced and preheated to 150-200°C. 160 g of the catalytically active material was

supported by spraying the catalyst slurry on it whil rotating the drum and the contents of the drum wer calcined under an air atmosphere at 520°C for 4 hours to obtain catalyst-I.

Separately, catalyst-J was prepared by the same method as in catalyst-I except that cesium nitrate was not added.

Into a carbon steel tube (ID = 20 mm, L = 4.5 meters) immersed in a salt bath maintained at 380°C, catalyst-J was first loaded to a height of 2,000 mm and onto it catalyst-I was loaded to a height of 2,000 mm.

From the top of the tube a 4-isopropyl-pseudo-cumene/air mixture of which the ratio of 4-isopropyl-pseudocumene/air was 40 g/NM^3 was introduced at a space velocity of 3,500 hr^{-1} to obtain pyromellitic anhydride in a yield of 98.7% by weight.

Example 14

$TiCl_4$ of special reagent grade (5,700 g) was gradually added dropwise to water to form a 60% aqueous solution. Sulfuric acid of special reagent grade (2,940 g) was added to the $TiCl_4$ aqueous solution with stirring. Separately, a saturated aqueous solution containing 3,940 g of ammonium sulfate of special reagent grade and heated to 100°C was prepared, and added to the $TiCl_4$-H_2SO_4 aqueous solution with stirring. The mixture was then left to stand to precipitate ammonium titanyl sulfate [$(NH_4)_2SO_4 \cdot TiOSO_4 \cdot H_2O$]. The precipitate was separated by filtration, and calcined at 750°C for 10 hours to obtain 2,300 g of TiO_2.

Oxalic acid (514 g) was dissolved in 6,400 cc of deionized water to form an oxalic acid solution, and 120 g of antimony trioxide and an aqueous solution of hydrogen chloride containing 257 g of ammonium vanadate, 16.2 g of ammonium dihydrogen phosphate and 12.2 g of niobium chloride were added to the oxalic acid solution. To the resulting solution were added 120 g of silicon nitride whiskers having a diameter of 0.5 micron, and an average

length of 180 microns and 1,800 g of TiO_2 mentioned above, and the mixture was stirred for 30 minutes to form a catalyst slurry.

Two thousand cc of an SiC carrier having an average particle diameter of 5 mm, an apparent porosity of 20% and an SiC content of 98.5% was introduced into an externally heatable rotatory drum, and preheated to 200 to 250°C. While the rotatory drum was rotated, the catalyst slurry was sprayed onto the carrier to deposit 180 g of the catalytically active material, and then calcined in air at 530°C for 8 hours. The finished catalyst had the following composition by weight.

$$V_2O_5:TiO_2:P_2O_5:Nb_2O_5:Sb_2O_3 = 10:90:0.5:0.3:6$$

The whisker content of the catalyst was 6% by weight based on the weight of the catalytically active material. The ratio of the catalytically active material effectively supported on the carrier based on its amount originally used was 94%.

Measurement of the pore distribution of the finished catalyst by a porosimeter in accordance with the mercury penetration method showed that the volume of pores having a diameter of 0.05 to 0.45 micron is 93% of the total volume of pores having a diameter of not more than 10 microns.

A stainless steel reaction tube having a diameter of 25 mm was filled with 100 cc of the resulting catalyst, and immersed in a molten salt bath kept at 390°C. Fifteen grams of durene and 500 Nℓ of air were passed hourly through the reaction tube and reacted. The reaction gas was conducted to a crystal collector and a scrubbing vessel to collect the product. The entire product collected was dissolved in warm water and analyzed. It was found that pyromellitic acid was obtained in a yield of 114.8% calculated as pyromellitic anhydride.

When the above procedure was repeated without adding the whiskers, the ratio of the catalytically active

material ffectively supported on the carrier was 63%, and the yield of pyromellitic anhydride was 113.2%.

Example 15

Zirconyl nitrate was thermally decomposed at 750°C for 3 hours to obtain ZrO_2 having a specific surface area of 25 m^2/g. ZrO_2 was finely pulverized to an average particle diameter of 0.2 micron and used as a catalyst material.

Oxalic acid (200 g) was dissolved in 6,400 cc of deionized water, and 96.7 g of ammonium metavanadate, 9.1 g of ammonium dihydrogen phosphate, 22.9 g of niobium chloride and 3.47 g of potassium hydroxide were added. Furthermore, 75 g of silicon carbide whiskers having a diameter of 0.2 micron and a length of 20 microns were added. The mixture was thoroughly stirred, and 1,800 g of the finely pulverized ZrO_2 prepared above was added by using an emulsifier, a catalyst slurry was obtained.

Two thousand cc of a ring-like carrier composed of 2% by weight of Al_2O_3, 6% by weight of SiO_2 and 92% by weight of SiC and having an apparent porosity of 45%, a specific surface area of 0.2 m^2/g, an average inside diameter of 4 mm, an average outside diameter of 6 mm and an average length of 6 mm was introduced into an externally heatable rotatory drum, and preheated to 150 to 200°C. The catalyst slurry prepared above was sprayed onto the carrier to deposit 180 g of the catalytically active material, and calcined in air at 540°C for 6 hours to obtain a catalyst. The whisker content of the catalsyt was 4% by weight based on the catalytically active material. The ratio of the catalytically active material effectively supported was 95%.

The resulting catalyst was filled to a height of 2.5 m in an iron reaction tube, 25 mm in inside diameter and 3.5 m in length, immersed in a molten salt bath kept at 400°C.

A gaseous mixture of durene and air having a

durene/air rati of 25 g/NM^3 was preheated to 140°C, and passed into the reactor from its top at a space velocity of 4,000 hr^{-1} (STP). Pyromellitic anhydride was obtained in an initial yield of 115.5% by weight. The hot spot temperature was 461°C.

Under these conditions, the reaction ws continued, and the hot spot temperature and the yield were measured at the end of 3 months and 6 months, respectively, and found to be 462°C and 115.4%, and 457°C and 115.0% by weight.

The activity of the catalyst was stable during this operation over extended periods of time.

When a catalyst was prepared in the same way as above except that the whiskers were not added, the ratio of the catalytically active material effectively supported was 64%. When the same reaction as above was carried out using the resulting catalyst, the initial yield of pyromellitic anhydride was 114.5% by weight, and hot spot temperature was 465°C. When the reaction was continued under these conditions, the hot spot temperature and the yield of the product were 466°C and 114.1% by weight, and 461°C and 113.3% by weight at the end of 3 months and 6 months, respectively.

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What we claimed is:

1. A supported catalyst on an inert carrier suitable for the preparation of pyromellitic acid or its anhydride by catalytic vapor phase oxidation of a tetra-C_1-C_4-alkylbenzene, said catalyst comprising catalytically active material composed of 1 to 20 parts by weight of V_2O_5, 99 to 80 parts by weight of TiO_2 and/or SnO_2 and/or ZrO_2, and per one hundred parts by weight of V_2O_5, TiO_2 and/or SnO_2 and/or ZrO_2, 0.02 to 10 parts by weight, calculated as P_2O_5, of a phosphorus compound, 0.01 to 5 parts by weight, calculated as Nb_2O_5, of a niobium compound, 0 to 1.2 parts by weight, calculated as oxide, of at least one metal selected from the group consisting of potassium, cesium, rubidium and thallium, and 0 to 10 parts by weight, calculated as Sb_2O_3, of an antimony compound, and an inert carrier supporting said catalytically active material thereon.

2. A supported catalyst on an inert carrier suitable for the preparation of pyromellitic acid or its anhydride by catalytic vapor phase oxidation of a tetra-C_1-C_4-alkylbenzene, said catalyst comprising a catalytically active material composed of 1 to 20 parts by weight of V_2O_5, 99 to 80 parts by weight of TiO_2, and per one hundred parts by weight of V_2O_5 and TiO_2, 0.02 to 10 parts by weight, calculated as P_2O_5, of a phosphorus compound, 0.01 to 5 parts by weight, calculated as Nb_2O_5, of a niobium compound, and 0.01 to 10 parts by weight, calculated as Sb_2O_3, of an antimony compound, and an inert carrier supporting said catalytically active material thereon.

3. A supported catalyst on an inert carrier suitable for the preparation of pyromellitic acid or its anhydride by catalytic vapor phase oxidation of a tetra-C_1-C_4-alkylbenzene, said catalyst comprising catalytically active material composed of 1 to 20 parts by weight of V_2O_5, 99 to 80 parts by weight of TiO_2 and SnO_2, and per

one hundred parts by weight of V_2O_5, TiO_2 and SnO_2, 0.02 to 10 parts by weight, calculated as P_2O_5, of a phosphorus compound, 0.01 to 5 parts by weight, calculated as Nb_2O_5, of a niobium compound, 0 to 1.2 parts by weight, calculated as oxide, of an oxide of at least one metal selected from the group consisting of potassium, cesium, rubidium and thallium, and 0 to 10 parts by weight, calculated as Sb_2O_3, of an antimony compound, and an inert carrier supporting said catalytically active material thereon.

4. The supported catalyst of claim 3 wherein the weight ratio of TiO_2 to SnO_2 is less than 4.

5. A supported catalyst on an inert carrier suitable for the preparation of pyromellitic acid or its anhydride by catalytic vapor phase oxidation of a tetra-C_1-C_4-alkylbenzene, said catalyst comprising catalytically active material composed of 1 to 20 parts by weight of V_2O_5, 99 to 80 parts by weight of TiO_2, SnO_2 and ZrO_2, and per one hundred parts by weight of V_2O_5, TiO_2, SnO_2 and ZrO_2, 0.02 to 10 parts by weight, calculated as P_2O_5, of a phosphorus compound, 0.01 to 5 parts by weight, calculated as Nb_2O_5, of a niobium compound, 0 to 1.2 parts by weight, calculated as oxide, of at least one metal selected from the group consisting of potassium, cesium, rubidium and thallium, and 0 to 10 parts by weight, calculated as Sb_2O_3, of an antimony compound, and an inert carrier supporting said catalytically active material thereon.

6. The supported catalyst of claim 5 wherein the weight ratio of TiO_2 + SnO_2 to ZrO_2 is less than 4.

7. The supported catalyst of any one of claims 1 to 6 wherein said insert carrier is porous and having an alumina content of not more than 10% by weight and a silicon carbide content of at least 50% by weight.

8. A supported catalyst according to any one of claims 1 to 7 which is prepared by using 1 to 20% by weight of the catalytically active material, of whiskers having an average diameter of not more than 5 microns and an aspect ratio of from 10 to 500 as a supp rting aid.

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Bitte in der Antwort stets angeben
Please refer to in your reply

August 9, 1985

Re: European patent application 85 106 175.4
Nippon Shokubai Kagaku Kogyo Co., Ltd.

Referring to Rule 88 EPC we are adding new pages 2, 5, 9, 11, 12, 13, 14, 17 and 23 (in tripl.) of the description which are intended to replace the corresponding pages as originally filed. In the new pages, we have carried out the following amendments of obvious errors:

Page 2, line 18:	fixd = fixed
Page 5, line 22:	0.15 = 0.05
Page 5, line 25:	mcirons = microns
Page 9, line 29:	ferric = ferrous
Page 11, ex. 5:	(Zn) = (ZnO)
Page 12, line 9:	dihydrogen = hydrogen
Page 12, line 19:	after "the drum" inserted "and calcining it at 550°C for 6 hours under an air atmosphere"
Page 13, line 11:	hydrogen = dihydrogen
Page 13, line 15:	60 m^2/g = 20 m^2/g
Page 13, line 28:	after "405°C" inserted "the catalyst was loaded to a height of 2.5 meters and"
Page 13, line 35:	dihydrogen = hydrogen
Page 14, line 33:	diammonium hydrogen = ammonium dihydrogen

Page 17, line 23: after "vanadate," inserted "36.4 g of ammonium dihydrogen phosphate"

Page 23, line 30: insert = inert

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EUROPEAN SEARCH REPORT

0163231

Application number

EP 85 10 6175

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	US-A-3 684 741 (FRIEDRICHSEN et al.) * Claim 1; column 2, lines 27-39,48-51; column 3, lines 31-32 *	1-7	C 07 C 51/265 C 07 C 63/313 C 07 D 493/04 // B 01 J 27/18
X	US-A-3 894 971 (REUTER et al.) * Claim 1; column 1, lines 45-53; column 3, lines 26-28 *	1-7	
X	US-A-3 925 425 (DRAGUEZ DE HAULT et al.) * Claims 1,5,6; column 3, line 64 - column 4, line 6 *	1-7	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 07 C 51/00 C 07 C 63/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	16-08-1985	KLAG M.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : techn logical background
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